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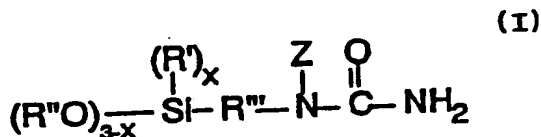
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(54) Title: MOISTURE CURABLE RTV SILICONE FORMULATION EMPLOYING  $\gamma$ -UREIDO-PROPYLTRIALKOXY-SILANE ADHESION PROMOTER



(57) Abstract

A one-component moisture curable RTV silicone containing as adhesion promoter a compound of formula (I) where R' is a one-to-seven carbon atom monovalent hydrocarbon group, R'' is a monovalent hydrocarbon radical, optionally interrupted by one or more ether oxygen atoms, R''' is a divalent hydrocarbon radical and x is 0 or 1, has particularly good bonding properties to metals, especially in hot oily environments such as automotive engine gasketing applications.

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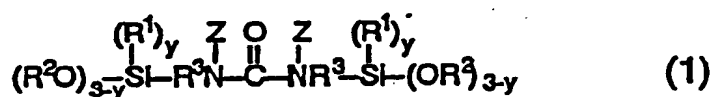
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<sup>+</sup> Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

**MOISTURE CURABLE RTV SILICONE FORMULATION  
EMPLOYING  $\gamma$  UREIDO-PROPYLTRIALKOXYSILANE ADHESION PROMOTER**

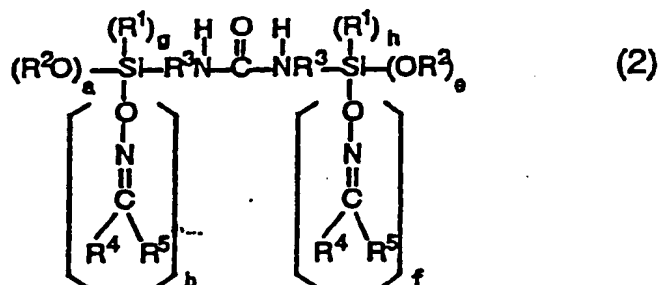
Background of the Invention

In US 4,506,058 there are disclosed certain moisture curable RTV  
5 silicone formulations which employ as an adhesion promoter a urea compound of  
the formula:



where  $R^1$  is a  $C_{(1-7)}$  monovalent hydrocarbon radical;  $R^2$  is a  $C_{(1-4)}$  alkyl radical,  $C_{(1-4)}$   
acyl radical or a radical of the formula  $-CH_2CH_2O)_nR^4$ , where  $n$  is 1 or 2 and  $R^4$  is  
10 a  $C_{(1-4)}$  alkyl radical.  $R^3$  is a  $C_{(1-10)}$  divalent hydrocarbon radical free of aliphatic  
unsaturation attached to a nitrogen atom of the urea nucleus through a non-  
aromatic carbon atom,  $Z$  is hydrogen or a  $C_{(1-4)}$  alkyl radical and  $y$  equals 0 or 1.

In US 4,847,396 there is disclosed a moisture curable RTV silicone  
formula employing a urea compound of the formula:



15

where  $R^1$ ,  $R^2$  and  $R^3$  are similarly defined,  $R^4$  and  $R^5$  are H, hydrocarbyl or  
halohydrocarbyl,  $g$  and  $h$  are 0 or 1, and  $a+b+g = f+g+h = 3$ .

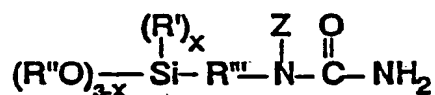
In US 3,671,562 there is described compound:



and related mono urea compounds. Such compounds are disclosed as coupling agents for improving bonding of organic polymers to glass substrates. Use of  
 5 these compounds in RTV silicone formulations or for bonding to metal substrates is not suggested by this reference.

#### Summary of the Invention

It has now been discovered that the urea compounds disclosed in US  
 10 3,675,562 may be employed as adhesion promoters in RTV silicone substrates giving superior metal bonding performance to the bis-silyl urea compounds of US 4,506,058 and 4,847,396, in similar formulations. Therefore, in one aspect there is provided a moisture curing RTV silicone formulation employing an adhesive promoting effective amount of a compound of the formula:



15

where R' is a one-to-seven carbon atom monovalent hydrocarbon group, R'' is a monovalent hydrocarbon radical, optionally interrupted by one or more ether oxygen atoms, R''' is a divalent hydrocarbon radical and x is 0 or 1.

In a still further aspect there is provided a process for bonding or  
 20 sealing metal substrates comprising applying a composition as just described, between the substrates, and then joining the substrates in the presence of moisture until bonded.

Detailed Description of the Invention

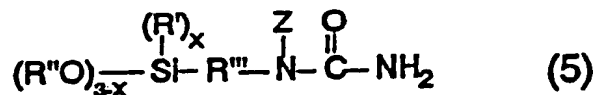
In accordance with the present invention there is provided a silicone composition which is storage stable in the substantial absence of moisture and which composition vulcanizes at room temperature on exposure to moisture comprising in admixture:

5 A) a reactive polyorganosiloxane consisting essentially of repeating units of the formula:



where R is a hydrocarbon or halohydrocarbon group, said reactive polyorganosiloxane having moisture curable end groups thereon,

10 B) a cure inducing effective amount of a condensation catalyst, and  
C) an adhesion promoting effective amount of a compound of the formula:



15 where R' is a one-to-seven-carbon atom monovalent hydrocarbon group, R'' is a monovalent hydrocarbon radical, optionally interrupted by one or more ether oxygen atoms, R''' is a divalent hydrocarbon radical and x is 0 or 1.

Generally polyorganosiloxane (A) can be any polyorganosiloxane consisting essentially of repeating units of formula (1) and which is terminated with radicals which will effect crosslinking upon exposure to moisture. Such polyorganosiloxanes are well known to those skilled in the art, but of particular interest in the present invention are polyorganosiloxanes wherein the silicone at each chain end is silanol terminated. Suitably the polyorganosiloxane (D) is a

silanol terminated polydimethylsiloxane which has a viscosity at 25° C of 2,000 cps - 250,000 cps, preferably about 4,000 cps to about 50,000 cps.

Effective amounts of condensation catalysts which can be used in the practice of the present invention to facilitate the cure of the room temperature vulcanizable compositions are, for example, from about 0.001% to about 1% based on the weight of polyorganosiloxane (A). Preferably the condensation catalyst is a tin compound such as dibutyltin dilaurate, dibutyltin diacetate, dibutyltin dimethoxide, stannous octoate, stannous oleate, stannous naphthenate and the like. Dimethyltin bis-neodecanoate is particularly preferred.

Titanium compounds which can be used are, for example, 1,3-propanedioxytitanium bis(ethylacetoacetate); 1,3-propanedioxytitanium bis(acetylacetonate); diisopropoxytitanium bis(acetylacetonate); titanium naphthenate, tetrabutyl titanate and the like. In addition, beta-dicarbonyltitanium compounds as shown in Weyenberg, U.S. Patent No. 3,334,067, can be used as condensation catalysts in the present invention. Additional catalysts which are well known in the art are provided in a rather exhaustive list in US 4,395,526, White et al. Of course, there may be utilized mixtures of suitable condensation catalysts.

The present invention is based on the surprising discovery that a self-bonding room temperature vulcanizable composition is obtained when an effective amount of a mono-silyl urea compound of formula (5) is also included in the RTV composition. Generally an effective amount of adhesion promoter of formula (5) will range from about 0.05 to about 10 parts by weight per 100 parts by weight of polyorganosiloxane (A).

As indicated hereinabove, it is necessary that the bis-silyl urea adhesion promoter of the present invention have two or three OR<sup>n</sup> radicals bonded to each silicon atom. Also it is preferable that R<sup>n</sup> be a methyl or ethyl group; e.g. each silicon atom preferably has three methoxy or ethoxy radicals bonded thereto. However, R<sup>n</sup> can generally be any alkyl radical of 1 to 4 carbon atoms such as formyl, acetyl or propionyl; or any alkoxyethyl radical such as β-methoxyethyl, β-ethoxyethyl or β-butoxyethyl; or any radical of the formula -CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>R<sup>m</sup> where n is 1 or 2 and R<sup>m</sup> is a C<sub>(1-4)</sub> alkyl radical such as -CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub> or -CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>C<sub>4</sub>H<sub>9</sub>.



R', if present, can be any monovalent hydrocarbon radical of up to 7 carbon atoms such as methyl, ethyl, hexyl, vinyl, allyl, hexenyl, phenyl, cyclohexyl, cyclopentyl and cyclopentenyl.

R'' can be any divalent hydrocarbon radical most suitably a C<sub>1</sub> - C<sub>6</sub> alkylene group.

There is also incorporated into the RTV composition of the invention a crosslinking silane compound. Various crosslinkers are known, all characterized by the presence of three or four hydrolyzable groups attached to the silane silicon atom. Most common are the trialkoxy, triamino, triacetoxo or trioxime substituted silanes. In the compositions of the invention trioxime silanes such as methyltris-methylethylketoximosilane or vinyltris-methylethylketoximosilane are preferred, suitably at levels of about 3 to about 9, preferably about 4 to about 6, ketoxime groups per silanol group.

The composition may also employ a plasticizer. Typically the plasticizer is a trimethylsilyl terminated dimethylsiloxane employed at levels of up to about 40% by weight of the composition.

In order to reinforce the polymer network as well as to impart non-sag properties to the system, a thixotropic agent is added to the overall composition. This agent which also adds physical strength to the system desirably is a treated or an untreated silica filler with a treated fumed silica filler being preferred. Treated or untreated silica fillers are well known to the art and generally any such conventional filler can be utilized. Suitable levels range from about 0.1% to about 5% by weight of the compositions. Typically, the silica filler has a very high surface area such as about 100-300M<sup>2</sup>/gram.

Optionally, from about 0.1 to about 5% by weight and preferably from about 0.2 to about 3% by weight based upon the total weight of the overall system or composition of a thermal aging additive can be utilized. This optional component functions to reduce oxidation and thermal rearrangement of polymers at elevated temperatures. These antioxidants may include materials like cerium neodecanoate, rare earth octoates and iron octoates. Representative samples can also usually include thermal aging additives such as carbon black, iron oxide powder, and titanium dioxide. Naturally, other pigments can be utilized.

Another optional ingredient is an inert non-reinforcing filler such as ground quartz, calcium carbonate, talc, clay, various silicate compounds and other materials well known in the art. The amount utilized is from about 5% to about 60% by weight bases upon the total weight of the sealant composition. Especially preferred fillers are stearic acid treated calcium carbonate fillers having particle sizes below about 0.06 microns, suitably 0.04-0.05 microns. Such fillers are commercially available and may be conveniently employed at levels of about 5% to about 70% of the total weight of the composition, preferably about 15% - 40% of the total composition.

In automotive engine sealant formulations another particularly useful filler is iron aluminum silicate which further improves the fluid immersion properties of the cured compositions particularly in engine coolant. A suitable filler is Ferrosil 14, sold by Kaopolite, Inc., Union, NJ, 98% of which has a particle size of 14 microns or less. Preserved levels of iron aluminum silicate range from 5% to 40% based on the total weight of the composition. The compositions of the invention may further comprise other additives known in the art such as pigments, odor masks or other additives known to improve the properties of RTV silicones for particular applications.

The compositions of the instant invention are formed by mixing the various ingredients together in the substantial absence of moisture. This mixing is carried out in the substantial absence of moisture because moisture will cause the ingredients to prematurely vulcanize. After mixing the composition is storage stable as long as moisture is prevented from contacting the composition. The physical properties of the composition will remain essentially unchanged for one year or more after packaging.

Compositions of this invention can also be utilized as a two component system. Such two component systems generally comprise as the basic ingredients as polyorganosiloxane base polymer and a filler in one package, and an alkyl silicate crosslinking agent mixed with a condensation catalyst as the second package. The compositions prepared in this manner are stored as such and when it is desired to cure the composition the two packages are mixed together and cured to form a silicon elastomeric composition.

The inventive formulations are especially useful in hot oily environments such as in automotive gasketing applications, where they give comparable or even improved properties compared to prior art formulations employing bis-urea compounds and existing commercial automotive gasketing silicones.

5 The invention may be illustrated by the following non-limiting examples.

### EXAMPLE 1

A composition of the invention was prepared as follows:

|    | <u>Component</u>   | <u>Weight<br/>Percent</u> |
|----|--|---------------------------|
| 10 | 6000 cps. silanol terminated polydimethylsiloxane                            | 38.62                     |
|    | 15 cs. M,D,T,OH Silicone Fluid <sup>1</sup>                                  | 5.80                      |
|    | 1000 cps. trimethylsilylterminated polydimethylsiloxane                      | 3.86                      |
|    | Hydrophobic stearic acid treated precipitated CaCO <sub>3</sub> <sup>2</sup> | 23.17                     |
|    | Iron Aluminum Silicate <sup>3</sup>  | 15.44                     |
| 15 | Hexamethyldisilazane treated fumed silica <sup>4</sup>                       | 3.86                      |
|    | Aluminum pigment   | 0.70                      |
|    | Vinyl tris-methylethylketoximosilane   | 6.49                      |
|    | $\gamma$ -ureidopropyltrimethoxysilane                                       | 2.00                      |
|    | <u>Dimethyltinbis-neodecanoate</u>   | <u>0.06</u>               |
| 20 |  | 100.00                    |

1 A plasticizer containing approximately 5 mole % trimethylsiloxy, 75 mole % dimethylsiloxy, 20 mole % methylsiloxy and 0.3 weight % OH

25 2 SoCal 322 from Kali-Chemie, Brussels, Belgium (0.04  $\mu$  average particle size)

3 Ferrosil 14, Kaopolite, Inc., Union, NJ

30 4 Zeothix 265, J.M. Huber Corporation, Havre de Grace, MD, treated with hexamethyldisilazane

The resulting RTV silicones were cured at 25° C, 50% relative humidity for 7 days. Lap shear adhesion was then measured (initial adhesion) and compared to results obtained on lap shears which had been immersed for 150 hours at 120° C in 5W-30 motor oil. Table 1 compares the results of these tests with lap shear results obtained when the monourea adhesion promoter was replaced with an equal weight

of Bis- $\gamma$ -trimethoxysilylpropyl urea (average of 3) and when competitive automotive RTV silicones were used. The data clearly shows that the adhesion of the invention composition actually increased during extended exposure to hot oil and giving final adhesion values even better than the bis-silyl urea containing formulation.

|    | Formulation   | Initial Steel Adhesion | 150 Hours in Hot Motor Oil | Percentage Change |
|----|---|------------------------|----------------------------|-------------------|
|    | <b><math>\gamma</math>-ureidopropyltrimethoxysilane</b> |                        |                            |                   |
|    | 1   | 265                    | 335                        | +35               |
|    | 2   | 315                    | 453                        | +44               |
| 5  | 3   | 250                    | 398                        | +59               |
|    | 4   | 260                    | 375                        | +44               |
|    | 5   | 213                    | 260                        | +22               |
|    | 6   | 250                    | 290                        | +18               |
|    | 7   | 285                    | 345                        | +21               |
| 10 | 8   | 260                    | 390                        | +56               |
|    | 9   | 265                    | 315                        | +19               |
|    | Average   | 263                    | 353                        | +25               |
|    | <b>COMPARATIVE FORMULATIONS</b>                         |                        |                            |                   |
|    | <b>Bis-trimethoxysilylpropylurea</b>                    |                        |                            |                   |
| 15 | A   | 350                    | 310                        | -11               |
|    | B   | 345                    | 320                        | -7                |
|    | C   | 353                    | 275                        | -20               |
|    | Average   | 349                    | 302                        | -14               |
| 20 | <b>Nissan 99MPA7007 D</b>                               |                        |                            |                   |
|    |   | 180                    | 190                        | +6                |
|    | <b>Mitsubishi MP997110 E</b>                            |                        |                            |                   |
|    |   | 150                    | 135                        | -10               |
|    | <b>Honda HC2963817 F</b>                                |                        |                            |                   |
|    |   | 115                    | 102                        | -11               |
| 25 | <b>Three Bond 1207E G</b>                               |                        |                            |                   |
|    |   | 160                    | 110                        | -31               |
|    | <b>Three Bond 1216 H</b>                                |                        |                            |                   |
|    |   | 180                    | 205                        | +14               |
| 30 | <b>Three Bond 1207D I</b>                               |                        |                            |                   |
|    |   | 155                    | 140                        | -10               |

**EXAMPLE 2**

A master batch silicone formulation J was prepared as follows:

|    | <u>Component</u>  | <u>Weight<br/>Percentage</u> |
|----|---|------------------------------|
| 5  | 20,000 cps silanol terminated polydimethylsiloxane      | 40.2                         |
|    | trimethylsilated silica                                 | 5.2                          |
|    | vinyl-tris-methylethylketoximosilane                    | 4.8                          |
|    | stearic acid treated calcium carbonate                  | 34.2                         |
| 10 | 1000 cps trimethylsilyl terminated polydimethylsiloxane | 15.5                         |
|    | dimethyltinbis-neodecanoate                             | 0.1                          |

To the master batch formulation J was added 1.46% by weight of the adhesion promoters listed in Table 2. Peel adhesions and cohesive failure % on aluminum lap shears, cured for 2 weeks at 25°C, 50% relative humidity, were determined and are recorded in Table 2 (each entry is an average of 2 tests).

**Table 2**

|    | Formulation | Adhesion Promoter                      | Peel Adhesion (PLI) Two Weeks | % Cohesive Failure Two Weeks |
|----|-------------|--|-------------------------------|------------------------------|
| 20 | J           | None                                   | 17.6                          | 24.2                         |
|    | K           | bis-trimethoxysilylpropylurea          | 38.0                          | 100.0                        |
|    | 10          | $\gamma$ -ureidopropyltrimethoxysilane | 37.9                          | 100.0                        |

25

**EXAMPLE 3**

A master batch as in Example 2 was prepared to which was added the adhesion promoters and amounts listed in Table 3. Peel adhesion and % cohesive failure on aluminum lap shears were determined as for the examples in Table 2 except that both one week and two week values were obtained. Results are shown in Table 3.

30

Table 3

| Formulation | Adhesion Promoter/<br>(Amount)                      | Peel Adhesive<br>(PLI) |              | % Cohesive<br>Failure |              |
|-------------|---|------------------------|--------------|-----------------------|--------------|
|             |   | One<br>Week            | Two<br>Weeks | One<br>Week           | Two<br>Weeks |
| M           | Bis-trimethoxysilylpropylurea<br>(1.46%)            | 29.9                   | 31.0         | 100                   | 100          |
| 11          | $\gamma$ -ureidopropyltrimethoxy-<br>silane (0.5%)  | 47.3                   | 41.5         | 100                   | 99           |
| 12          | $\gamma$ -ureidopropyltrimethoxy-<br>silane (1.0%)  | 41.0                   | 36.7         | 100                   | 100          |
| 13          | $\gamma$ -ureidopropyltrimethoxy-<br>silane (1.47%) | 27.2                   | 30.8         | 86                    | 98           |

**EXAMPLE 4**

Specimens were prepared from the formulations prepared in Example 3 according to ASTM D-412, Die C, after 1 week curing at 25°C, 50% relative humidity. Physical property testing results on these samples (initial values) and on cured specimens which were subsequently immersed in 50°C motor oil for 1 week (final values) are reported in Table 4. The results show good property retention under the test condition.

12

Table 4

## Hot Oil Stability Tests with N(Trimethoxysilylpropyl) Urea

| 5  |                           | Formulations |        |        |        |
|----|---------------------------|--------------|--------|--------|--------|
|    |                           | M            | 11     | 12     | 13     |
|    | Original Shore A          | 31           | 27     | 28     | 31     |
|    | Final Shore A             | 16           | 16     | 14     | 17     |
|    | (%) Change in Shore A     | (48.4)       | (41.0) | (50.0) | (45.2) |
|    |                           |              |        |        |        |
| 10 | (%) Volume Swell          | 24.7         | 25.5   | 27.1   | 27.2   |
|    |                           |              |        |        |        |
|    | Orig. Tensile(ave) (psi)  | 253.9        | 264.8  | 254.1  | 268.0  |
|    | Final Tensile(Ave) (psi)  | 182.7        | 168.7  | 152.8  | 147.3  |
|    | (%) Change in Tensile     | (28.1)       | (36.3) | (39.9) | (45.0) |
| 15 |                           |              |        |        |        |
|    | Orig. Elongation(Ave) (%) | 430.0        | 513.3  | 450.0  | 416.7  |
|    | Final Elongation(Ave) (%) | 506.7        | 445.0  | 427.0  | 420.0  |
|    | (%)Change in Elongation   | 17.8         | (13.3) | (5.1)  | (0.8)  |

20



**EXAMPLE 5**

A RTV silicone master batch formulation was prepared as follows:

|    | <u>Component</u>                                       | <u>Weight ..<br/>Percentage</u> |
|----|--|---------------------------------|
| 5  | 5000 cps silanol terminated polydimethylsiloxane       | 39.4                            |
|    | 15 cs. M,D,T,OH Silicone Fluid                         | 5.9                             |
|    | 1000 cps trimethylsilylterminated polydimethylsiloxane | 3.9                             |
|    | Hydrophobic calcium carbonate                          | 23.7                            |
|    | Iron aluminum silicate                                 | 15.8                            |
| 10 | Aluminum pigment                                       | 0.7                             |
|    | Treated silica   | 3.9                             |
|    | Vinyl tris-methylethylketoximosilane                   | 6.6                             |
|    | <u>Dimethyltinbis-neodecanoate</u>                     | <u>0.06</u>                     |

15 The polymer, plasticizers, fillers and pigments were mixed together under high shear mixing conditions in a vertical change can mixer at 120°C under vacuum for three hours. The batch was then cooled and the vinyltris-methylethylketoximosilane and tin catalyst added in sequence.

20 To two portions of this master batch were added 2.0 wt %  $\gamma$ -ureidopropyltrimethoxysilane and 2.0 wt % bis-trimethoxysilylpropyl urea, respectively. Table 4 gives the results of testing the respective cured formulations after initial curing, immersion in hot 5W-30 motor oil (150 hrs at 120°C) or immersion in hot engine coolant (150 hrs., 100°C). The shear adhesion values are  
25 determined on Honda cold-rolled steel lap shears.

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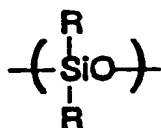
Table 5

| Adhesion/Promoter                      | Initial | 150 hrs @<br>120°C in<br>5W-30 | 150 hrs. @<br>100°C in<br>Coolant |
|--|---------|--------------------------------|-----------------------------------|
| None                                   |         |                                |                                   |
| Shore A, hardness                      | 37      | 26                             | 23                                |
| Tensile, psi                           | 386     | 355                            | 192                               |
| Elongation, %                          | 380     | 300                            | 450                               |
| Shear Adhesion, psi                    | 203     | 245                            | 120                               |
| Bis-trimethoxysilylpropyl urea         |         |                                |                                   |
| Shore A, hardness                      | 41      | 32                             | 24                                |
| Tensile, psi                           | 358     | 376                            | 194                               |
| Elongation, %                          | 310     | 330                            | 410                               |
| Shear Adhesion, psi                    | 350     | 310                            | 120                               |
| $\gamma$ -ureidopropyltrimethoxysilane |         |                                |                                   |
| Shore A, hardness                      | 42      | 30                             | 31                                |
| Tensile, psi                           | 372     | 383                            | 264                               |
| Elongation, %                          | 320     | 300                            | 470                               |
| Shear adhesion, psi                    | 273     | 350                            | 180                               |

## WHAT IS CLAIMED IS:

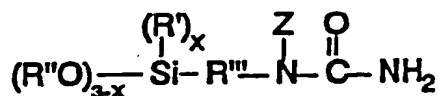
1. A moisture curing room temperature vulcanizing silicone composition comprising in admixture:

5 A) a reactive polyorganosiloxane consisting essentially of repeating units of the formula



where R is a hydrocarbon or halohydrocarbon group, said reactive polyorganosiloxane having moisture curable end groups thereon,

10 B) a cure inducing effective amount of a condensation catalyst, and  
C) an adhesion promoting effective amount of a compound of the formula



15 where R' is a one to seven carbon atom monovalent hydrocarbon group, R'' is a monovalent hydrocarbon radical, optionally interrupted by one or more ether oxygen atoms, R''' is a divalent hydrocarbon radical and x is 0 or 1.

2. A composition as in claim 1 wherein the polyorganosiloxane (A) is terminated with silanol groups.

20 3. A composition as in claim 2 wherein the silanol terminated polyorganosiloxane has a viscosity at 25°C of 2,000 - 250,000 cps.

4. A composition as in claim 1 wherein the condensation catalyst is a tin catalyst.

5. A composition as in claim 1 wherein the condensation catalyst is present in an amount of from 0.001% to 1% of the weight of polyorganosiloxane (A).
6. A composition as in claim 5 wherein the condensation catalyst is dimethyltinbis-neodecanoate.
7. A composition as in claim 1 wherein the adhesion promoter is present in an amount of from 0.005 to about 10% of the weight of polyorganosiloxane (A).
8. A composition as in claim 1 wherein x is 0.
9. A composition as in claim 1 wherein Z is H.
10. A composition as in claim 1 wherein the adhesion promoter is a  $\gamma$ -ureidopropyltrialkoxysilane.
11. A composition as in claim 10 wherein the adhesion promoter is  $\gamma$ -ureidopropyltrimethoxysilane.
12. A composition as in claim 1 further comprising a non-reinforcing filler in an amount of from about 5% to about 70% by weight of the composition.
13. A composition as in claim 12 wherein said filler is a hydrophobic calcium carbonate.
14. A composition as in claim 13 wherein the calcium carbonate filler has an average particle size of 0.04 - 0.05 microns.
15. A composition as in claim 1 further comprising 0.1% to about 5% by weight of a silica filler.
16. A composition as in claim 1 wherein the silica filler is a hydrophobic silica.

17. A composition as in claim 1 further comprising an iron aluminum silicate filler.

5 18. A composition as in claim 12 wherein the iron aluminum silicate filler is present at a level of between about 5% and 40% by weight of the composition.

10 19. A composition as in claim 1 further comprising a hydrophobic silica filler in an amount of about 0.1% - 5% by weight of the composition, a calcium carbonate filler having an average particle size of 0.04 - 0.05 microns in an amount of 15% - 40% by weight of the composition and an iron aluminum silicate filler in an amount of between about 5% and 20% by weight of the composition.

15 20. A composition as in claim 19 wherein the adhesion promoter is  $\gamma$ -ureidopropyltrimethoxysilane.

21. A composition as in claim 19 wherein the polyorganosiloxane (A) is a silanol terminated polydimethylsiloxane having a viscosity of between about 4,000 cps to about 50,000 cps at 25°C.

20 22. A composition as in claim 21 further comprising vinyltris-methylethylketoximosilane in an amount providing between about 3 and about 9 ketoxime groups per silanol group.

25 23. A composition as in claim 1 further comprising a crosslinking effective amount of vinyltris-methylethylketoximosilane.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/08122

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) <sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C08G 77/06

U.S. CL. 528/18

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

| Classification System | Classification Symbols |
|-----------------------|------------------------|
| U.S.                  | 528/18                 |

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>

| Category <sup>9</sup> | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>  | Relevant to Claim No. <sup>13</sup> |
|-----------------------|---|-------------------------------------|
| X                     | US, A, 4,506,058 (ASHBY ET AL)<br>19 MARCH 1985: See column 3, line 25 through<br>column 4, line 45.            | 1-23                                |
| X                     | US, A, 3,671,562 (PEPE ET AL) 20 JUNE 1972<br>See column 1, line 10 through column 3, line<br>10; EXAMPLES 1-5. | 1-23                                |

<sup>9</sup> Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

07 JANUARY 1992

International Searching Authority

Date of Mailing of this International Search Report

21 JAN 1992

Signature of Authorized Officer

*Michael J. Marquis*